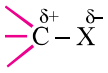
UNIT 10

HALOALKANES AND HALOARENES

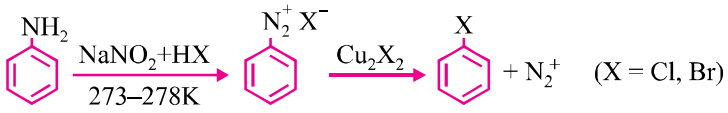
Points to Remember

1. Haloalkanes (Alkyl halides) are halogen derivatives of alkanes with general formula $[C_nH_{2n+1}X]$. (X = F, Cl, Br or I)
2. Haloarenes (Aryl halides) are halogen derivatives of arenes with general formula Ar – X.
3. Since halogen is more electronegative than C, hence C – X bond is polar.



4. **Named Reactions :**

(a) Sandmeyer Reaction :



(b) Finkelstein Reaction :

$$R - X + NaI \xrightarrow{\text{dry acetone}} R - I + NaX \quad (X = Cl, Br)$$

(c) Swartz Reaction :

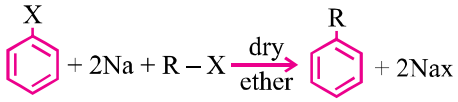
$$CH_3 - Br + AgF \rightarrow CH_3 - F + AgBr$$

Instead of Ag – F, other metallic fluoride like Hg_2F_2, CoF_2 or SbF_3 can also be used.

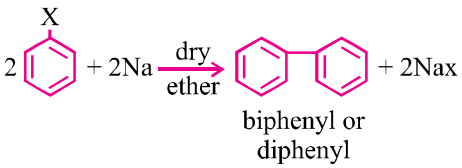
(d) Wurtz Reaction :

$$2R - X + 2Na \xrightarrow{\text{dry ether}} R - R + 2NaX$$

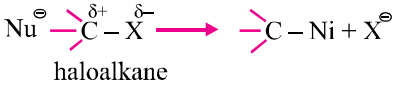
(e) Wurtz-Fittig Reaction :



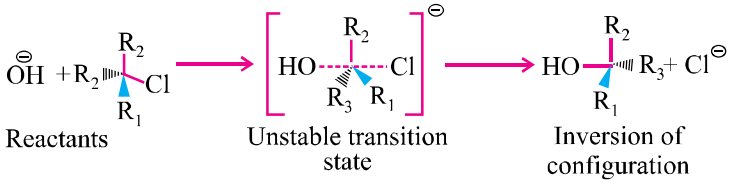
(f) Fittig Reaction :



5. Nucleophilic Substitution Reactions :



(a) Substitution nucleophilic bimolecular (S_N^2) :

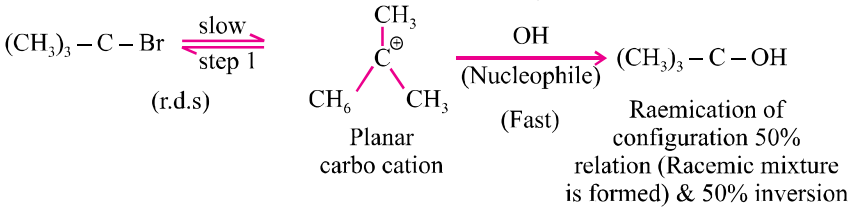


1. 1° haloalkane
2. Bimolecular, 2nd order
3. One step

Order of reactivity : 1° > 2° > 3°

Deciding factor : Steric hindrance

(a) Substitution nucleophilic unimolecular (S_N^1) :



1. 3° haloalkane
2. Unimolecular, 1st order
3. Two steps

Order of reactivity : 3° > 2° > 1°

Deciding factor : Stability of carbo cation

* Allylic $\left[CH_2=CH-\overset{\oplus}{C}H_2\right]$ and benzylic $\left[C_6H_5\overset{\oplus}{C}H_2\right]$ halides undergo reaction via SN^1 mechanism as the corresponding carbo cations are resonance stabilized.

6. Aryl halides are much less reactive towards nucleophilic substitution reactions than haloalkanes.

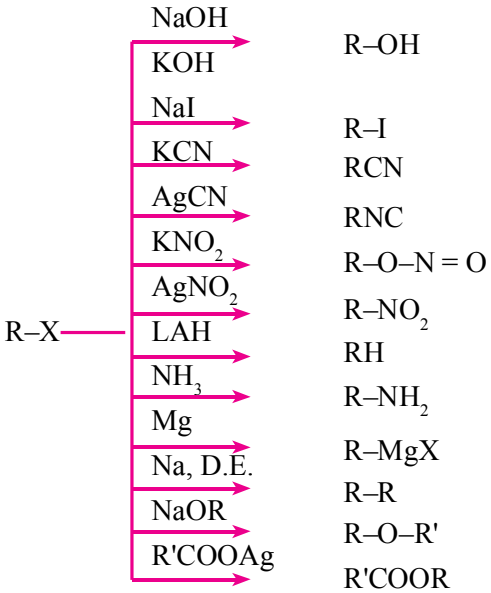
7. Halogen is deactivating but *o, p*-directing in electrophilic substitution reaction of haloarenes.

8. $CHCl_3$ is stored in dark bottles upto brim so that formation of poisonous gas phosgene in presence of air and light can be avoided.

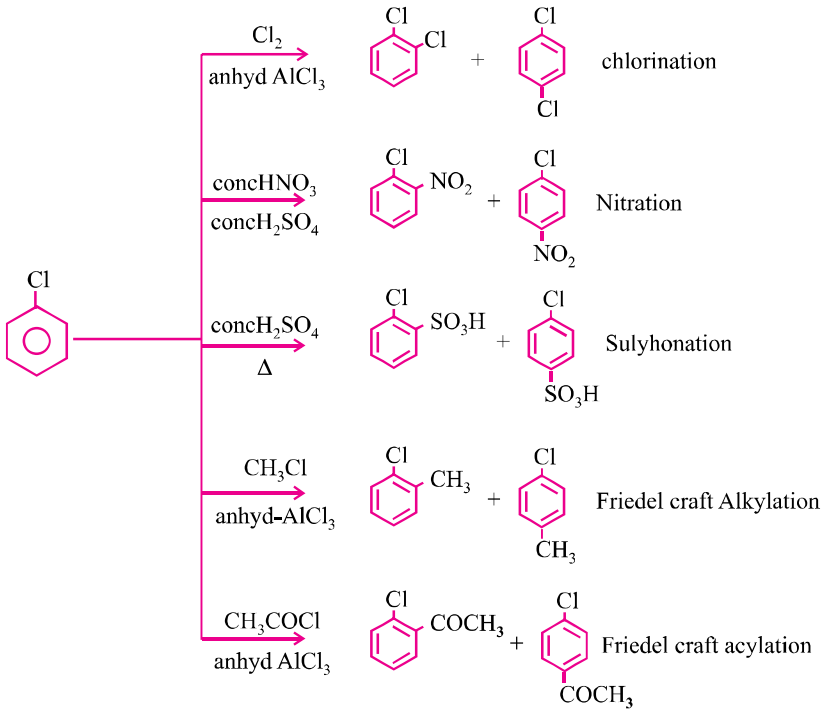
$$2CHCl_3 + O_2 \xrightarrow{\text{light}} 2COCl_2 + 2HCl$$

Chloroform Carbonyl chloride (phosgene)

9. Reaction of Haloalkanes :



10. Electrophilic Substitution Reaction of Haloarenes :



11. Distinguishing test for alkyl chlorides, bromides and iodide : Alkyl chlorides react with $AgNO_3$ to give white precipitate which is soluble in alcoholic ammonium hydroxide. Alkyl bromides react with $AgNO_3$ to give a yellow precipitate which is sparingly soluble in alcoholic ammonium hydroxide. Alkyl iodides react with $AgNO_3$ to give dirty yellow precipitate, which is insoluble in alcoholic ammonium hydroxide.

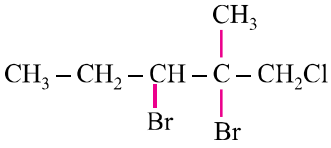
E.g., $CH_3 - Cl \xrightarrow[AgNO_3]{HNO_3} AgCl\downarrow$

White ppt.

Vinyl and aryl halides do not yield silver halide under these conditions.

VERY SHORT ANSWER TYPE QUESTIONS (1 Mark)

Q. 1. Give IUPAC name of :



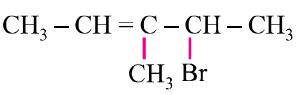
[*Hint :* 1-chloro-2, 3-dibromo-2-methyl pentane]

Q. 2. Identify A and B in each of the following processes :

$$CH_3CH_2Cl \xrightarrow{NaCN} A \xrightarrow[Ni/H_2]{Reduction} B$$

[*Hint :* A : $CH_3 - CH_2 - CN$; B : $CH_3CH_2CH_2NH_2$]

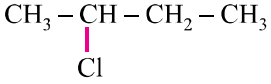
Q. 3. Draw the structure of 4-bromo-3-methylpent-2-ene.

[*Hint :* 

Q. 4. Why Grignard reagent should be prepared under anhydrous conditions ?

Q. 5. Chloroform is stored in dark coloured and sealed bottles. Why ?

Q. 6. An alkyl halide having molecular formula C_4H_9Cl is optically active. What is its structure ?

[*Hint* 

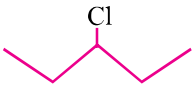
Q.7. An organic compound 'A' on treatment with KCN gave B which on hydrolysis with dil. HCl gave acetic acid. Identify A.

[*Hint :* A : CH_3Cl]

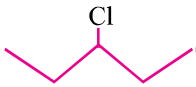
Q. 8. Write IUPAC name of iodoform.

[*Hint :* Triiodomethane]

Q. 9. Which one of the following two substances undergo SN^1 reaction faster and why ?



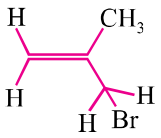
Or

(Hint : 

(3°)

Q. 10. Haloalkanes react with KCN to form alkyl cyanides as main product while AgCN form isocyanides as the chief product. Explain.

Q. 11. Write the IUPAC name of the following compound :



[*Hint :* 3-bromo-2-methylprop-1-ene]

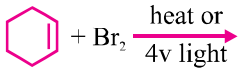
Q. 12. Arrange the following in order of their increasing reactivity in nucleophilic substitution reactions :

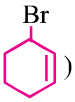
$$CH_3F,\ CH_3I,\ CH_3Br,\ CH_3Cl$$

[*Hint :* $CH_3F < CH_3Cl < CH_3Br < CH_3I$]

Q. 13. Allyl chloride is more reactive than n-propyl chloride towards nucleophilic substitution reaction. Explain why ?

Q. 14. Complete the reaction :



(Hint : 

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Q. 15. How will you convert 2-bromo propane into 1-bromo propane ?

Q. 16. Give one chemical test to distinguish between chlorobenzene and benzyl chloride ?

[*Hint :* $AgNO_3$ test]

Q. 17. Why iodoform show antiseptic properties ?

[*Hint :* Due to free liberated iodine.]

Q. 18. Optically active 2-iodobutane on treatment with NaI in acetone gives a product which does not show optical activity. Explain.

[*Hint :* Racemic mixture is obtained.]

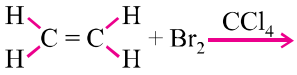
Q. 19. The presence of nitro group ($-NO_2$) at ortho or para positions increases the reactivity of haloarenes towards nucleophilic substitution reactions. Explain.

Q. 20. For the preparation of alkyl chlorides from alcohols, thionyl chloride ($SOCl_2$) is preferred. Give reason.

SHORT ANSWER-I TYPE QUESTIONS (2 Marks)

Q. 1. Complete the following reactions :

(i) $C_6H_5N_2Cl + KI \rightarrow$

(ii) 

Q. 2. Carry out the following conversions in not more than two steps :

(i) Toluene to benzyl alcohol

(ii) Benzyl alcohol to phenylethanenitrile

Q. 3. Give reasons :

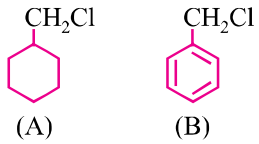
(i) Boiling point of alkyl bromide is higher than alkyl chloride.

(ii) Alkyl halides are better solvents than aryl halides.

[*Hint :* (i) High magnitude of van der Waal's forces in alkyl bromides.

(ii) C – X is more polar in haloalkanes.]

Q. 4. Which of the following compounds would undergo S_N^1 reaction faster and why ?



(A) (B)

Hint : (A)

Q. 5. Identify and indicate the presence of centre of chirality, if any, in the following molecules. How many stereoisomers are possible for those containing chiral centre :

(i) 1, 2-dichloropropane

(ii) 3-bromopent-1-ene

Q. 6. Convert :

(i) Benzene to m-nitrochlorobenzene

(ii) Benzene to diphenyl

Q. 7. What happens when :

(i) Propene is treated with HBr in presence of peroxide.

(ii) Benzene is treated with methyl chloride in presence of $AlCl_3$.

Q. 8. (i) An alkyl halide having molecular formula C_4H_9Cl is optically active. What is its structure ?

(ii) Alkyl iodides develop colouration on long standing particularly in light. Explain.

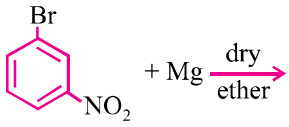
[*Hint :* (i) $CH_3 – CH(Cl) – CH_2 – CH_3$

(ii) Due to decomposition by light and produce I_2.]

Q. 9. Tert-butyl bromide reacts with aq. NaOH by S_N^1 mechanism while n-butylbromide reacts with S_N^2 mechanism. Why ?

Q. 10. Although chlorine is an electron withdrawing group, yet it is o, p-directing in electrophilic aromatic substitution reactions. Explain, why is it so ?

Q. 11. Identify the products :

(i) 

(ii) $CH_3-\underset{\underset{Br}{|}}{CH}-CH_3 \xrightarrow{\text{alc.KOH}} A \xrightarrow[H_2O_2]{HBr} B$

Q. 12. (i) Arrange the following halides in order of increasing S_N^1 reactivity :

CH_3Cl, CH_3Br, CH_3CH_2Cl, $(CH_3)_2CHCl$

(ii) Which out of 1-bromobutane & 2-bromobutane would react faster by S_N^2 pathway and why ?

Q. 13. Identify the products :

$$C_6H_6 \xrightarrow[\text{anhy. } AlCl_3]{CH_3Cl} A \xrightarrow[h\nu]{Cl_2\ (1\ \text{mole})} B \xrightarrow{KOH} C \xrightarrow{HBr} D$$

Q. 14. Carry out the following conversions :

(i) But-1-ene to n-butyliodide

(ii) Isopropyl alcohol to iodoform

Q. 15. An organic compound A reacts with PCl_5 to give compound B. Compound B reacts with Na/ether to give n-butane. What are compounds A and B ?

[*Hint :* A = C_2H_5OH, B = C_2H_5Cl]

Q. 16. Write short note on :

(i) Sandmeyer reaction

(ii) Finkelstein reaction

Q. 17. Name the reagents used to convert :

(i) 2-chloropropane to 2-nitropropane

(ii) Chloroethane to n-butane

[*Hint :* (i) $AgNO_2$

(ii) Na/dry ether]

SHORT ANSWER-II TYPE QUESTIONS (3 Marks)

Q. 1. Rearrange the compounds of each of the following sets in order of reactivity towards S_N^2 displacement :

(i) 2-bromo-2-methyl butane, 1-bromopentane, 2-bromopentane

(ii) 1-bromo-3-methylbutane, 2-bromo-2-methyl butane, 3-bromo-2-methyl butane

(iii) 1-bromobutane, 1-bromo-2, 2-dimethyl propane, 1-bromo-2-methyl butane

Q. 2. Answer the following :

(i) Haloalkanes easily dissolve in organic solvents, why ?

(ii) What is known as racemic mixture ? Give example.

(iii) Of the two bromo derivatives, $C_6H_5CH(CH_3)Br$ and $C_6H_5CH(C_6H_5)Br$, which one is more reactive in S_N^1 substitution reaction and why ?

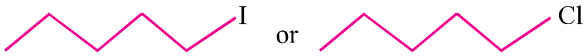
Q. 3. Answer the following :

(i) What is meant by chirality of a compound ? Give an example.

(ii) Which one of the following compounds is more easily hydrolysed by KOH and why ?

$CH_3CHClCH_3CH_3$ or $CH_3CH_2CH_2Cl$

(iii) Which one undergo S_N^2 substitution reaction faster and why ?



Q. 4. Complete the following reactions :

(i) $CH_3CH_2OH \xrightarrow{SOCl_2} A \xrightarrow{KCN} B$

(ii) $(CH_3)_2CHBr + Na \rightarrow$

(iii) $CH_3CH_2Cl \xrightarrow{AgNO_3}$

Q. 5. How the following conversions can be carried out ?

(i) But-1-ene to n-butyl iodide

(ii) Tert-butyl bromide to isobutyl bromide

(iii) Ethanol to but-1-yne

Q. 6. Write short notes on :

(i) Wurtz-Fittig reaction

(ii) Fittig reaction

(iii) Dehydrohalogenation reaction

Q. 7. An organic compound 'A' having molecular formula C_4H_8 on treatment with dil. H_2SO_4 give another compound 'B'. B on treatment with conc. HCl and anhy. $ZnCl_2$ gives 'C'. C on treatment with sodium ethoxide gives back 'A'. Identify the compound. Write the equations involved.

Q. 8. What happens when :

(i) 1-bromopropane reacts with metallic sodium.

(ii) Bromoethane is treated with caustic potash.

(iii) Iodomethane is treated with ammonia.

Q. 9. Identify A, B and C :

$$\text{2-propanol} \xrightarrow{SOCl_2} A \xrightarrow{Mg} B \xrightarrow{H_2O} C$$

Q. 10. Account for the following :

(i) A small amount of ethyl alcohol is added to $CHCl_3$ stored for use as an anaesthetic.

(ii) After using CCl_4 as a fire extinguisher inside a closed space, the space is thoroughly ventilated.

(iii) When 2-chloro-3-methylbutane is treated with alcoholic potash, 2-methyl-2-butene is the main product.

[*Hint :* (i) To convert harmful $COCl_2$ to ethyl carbonate.

(ii) To sweep out $COCl_2$ formed by CCl_4 vapour and H_2O vapour.

(iii) Saytzeff rule.

Q. 11. How will you distinguish between :

(i) Vinyl chloride and ethyl chloride

(ii) Chlorobenzene and cyclohexyl chloride

(iii) Ethyl chloride and ethyl bromide

Q. 12. Explain the following :

(i) The dipole moment of chloroethane is higher than that of chlorobenzene.

(ii) Although halo alkanes are polar in character yet they are insoluble in water.

(iii) Vinyl chloride is unreactive in nucleophilic substitution reactions.

Q. 13. (i) Which will have a higher boiling point ?

1-chloroethane or 2-chloro-2-methyl butane. Give reason.

(ii) p-chloronitrobenzene undergoes nucleophilic substitution faster than chlorobenzene. Explain giving resonating structure as well.

Q. 14. (i) What are ambident nucleophiles ? Explaine with an example.

(ii) Convert ethyl bromide to diethyl ether.

(iii) What are freons ?

Q. 15. A hydrocarbon 'A' (C_4H_8) is added with HBr in accordance with Markonikov's rule to give compound 'B' which on hydrolysis with aqueous alkali forms tertiary alcohol 'C' ($C_4H_{10}O$). Identify A, B and C.

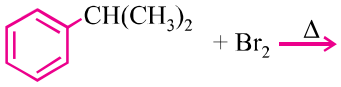
Q. 16. (i) Which isomer of C_4H_9Cl will have the lowest boiling point ?

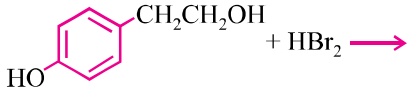
(ii) Predict the alkenes that would be formed by dehydrohalogenation with sodium ethoxide and ethanols. Predict major alkenes :

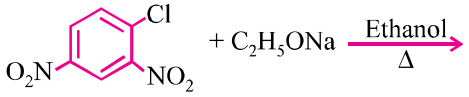
(a) 2-chloro-2-methylbutane

(b) 3-bromo-2, 2, 3-trimethylpentane

Q. 17. Write the structure of major product in each of the following :

(i) 

(ii) 

(iii) 

Q. 18. Write the main products when :

(i) n-butyl chloride is treated with alcoholic KOH

(ii) 2, 4, 6-trinitrochlorobenzene is subjected to hydrolysis.

(iii) Methyl chloride is treated with AgCN.

LONG ANSWER TYPE QUESTIONS (5 Marks)

Q. 1. How would you bring about the following conversions :

(i) Propene to 2-bromopropane

(ii) Bromoethane to propanoic acid

(iii) 1-chloropropane to 1-propanol

(iv) Ethanol to chloroethane

(v) 1-iodopropane to propene

Q. 2. What happens when : (Give chemical reactions)

(i) Cyclohexanol is treated with thionyl chloride

(ii) p-hydroxybenzyl alcohol is heated with HCl.

(iii) Ethyl bromide is refluxed with NaI in acetone.

(iv) Ethyl bromide is treated with mercurous fluoride.

(v) Chlorobenzene is subjected to hydrolysis.

Q. 3. Complete the following reactions :

(i) $C_6H_6 \xrightarrow{Cl_2/Fe} X \xrightarrow[\text{Pyridine, } \Delta]{CuCN} Y \xrightarrow{H^+, H_2O} Z$

(ii) $C_2H_4 \xrightarrow{HBr} X \xrightarrow{\text{aq. KOH}} Y \xrightarrow{I_2, NaOH} Z$

(iii) $CH_3CH_2Br \xrightarrow{AgCN} A$

(iv) 3-ethylpent-2-ene $\xrightarrow{Br_2/H_2O}$ B

Q. 4. Account for the following :

(i) Sulphuric acid is not used during the reaction of alcohols with KI.

(ii) p-methoxybenzyl bromide reacts faster than p-nitrobenzyl bromide with ethanol to form an ether product.

(iii) Organic halogen compounds used as solvents in industry are chlorides rather than bromides and iodides.

(iv) Wurtz reaction fails in case of tert-alkyl halides.

(v) Alkyl halides are insoluble in water though they contain a polar C – X bond.

(vi) Use of $CHCl_3$ as anaesthetic is not preferred.

Q. 5. (i) A primary alkyl halide (A), C_4H_9Br reacted with hot alcoholic KOH to give compound (B). Compound (B) reacted with HBr to give (C), which is an isomer of (A). When (A) was reacted with sodium metal, it gave a compound (D), C_8H_{18} which was different than the compound when n-butyl bromide was reacted with sodium. Give the structural formula of (A) and write equations of all the reactions.

(ii) Iodoform gives a precipitate with $AgNO_3$ on heating while $CHCl_3$ does not. Why ?

[*Hint :* A : $\Rightarrow CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2Br$]

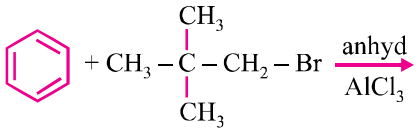
HOTS

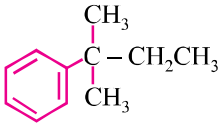
Q. 1. Why alkyl halides are generally not prepared in laboratory by free radical halogenations of alkanes ?

Q. 2. Hydrolysis of 2-bromo-3-methylbutane (2°) gives only α-methyl-2-butanol (3°). Explain.

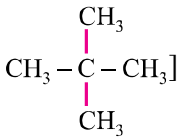
Q. 3. Write major product of the following reactions :

(i) $CH_2 = CH - Br \xrightarrow[\text{ethanol}]{AgCN}$

(ii) 

[*Hint :* (i) No reaction (ii) ]

Q. 4. A hydrocarbon of molecular mass 72 g mol^{-1} gives a single monochloro derivative and two dichloro derivatives on photochlorination. Give the structure of the hydrocarbon.

[*Hint :* ]

Q. 5. Cyanide ion acts as an ambident nucleophile. From which end it acts as a stronger nucleophile in aqueous medium ? Give reason for your answer.

MULTIPLE CHOICE QUESTIONS

Q. 1. The chiral compound is :

(a) 3-chloropentane (b) Propene

(c) 2-chloropropane (d) 2-chlorobutane

Ans. (d)

Q. 2. Chloroethane on heating with alcoholic KOH gives :

(a) Ethane (b) Ethene

(c) Ethyne (d) Ethyl alcohol

Ans. (b)

Q. 3. Phosgene is a common name for :

(a) Phosphoryl chloride (b) Carbonyl chloride

(c) Carbon dioxide & phosphine (d) Carbon tetrachloride

Ans. (b)

Q. 4. Which of the following possesses highest melting point ?

(a) Chlorobenzene (b) n-dichlorobenzene

(c) o-dichlorobenzene (d) p-dichlorobenzene

Ans. (d)

Q. 5. KCN reacts readily to form a cyanide with :

(a) Ethyl alcohol (b) Ethyl bromide

(c) Bromobenzene (d) Chlorobenzene

Ans. (b)

VALUE BASED QUESTIONS (4 Marks)

Q. 1. Chlorofom is a colourless oily liquid with a peculiar smell. It is sparingly soluble in water. The vapour when enhaled cause unconsciousness and therefore, it is used as anaesthetic.

Answer the following questions :

(i) What happens when $CHCl_3$ is not protected from O_2 during its storage ?

(ii) Why is the use of $CHCl_3$ as an anaesthetic has been reduced ?

Q. 2. DDT is one of the most powerful insecticide which is effective against the mosquitoes that spread malaria. Mukesh's mother wanted to buy DDT from the market to use at night but Mukesh stopped her.

(i) Why did Mukesh stopped her mother for using DDT at night ?

(ii) What values are attached to Mukesh's suggestion ?